FIRE EXTINGUISHING METHODS USING FLUORINATED HYDROCARBONS

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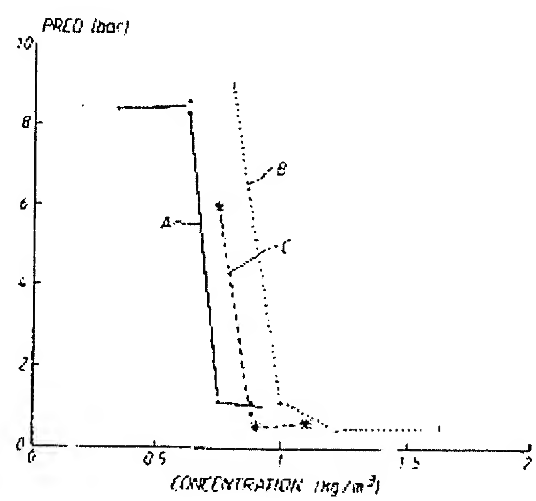
A fire extinguishing and explosion suppression agent is disclosed comprising perfluorohexane discharged in atomised form, such as, for example, by means of a pressurising gas which may, for instance, be nitrogen at least partially dissolved in the perfluorohexane. Another agent disclosed comprises a mixture of trifluoromethane dissolved in perfluorohexane. The agents disclosed have zero ozone depletion potential and low toxicity.



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(56) Documents cited
EP 0460990 A1 WO 92/01491 A1 WO 91/02564 A

(58) Field of search
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(54) **Fire extinguishing methods using fluorinated hydrocarbons**

(57) A fire extinguishing and explosion suppression agent is disclosed comprising a partially or fully fluorinated hydrocarbon having a boiling point above 0°C, for example, perfluorohexane, discharged in atomised form, such as, for example, by means of a pressurising gas which may, for instance, be nitrogen at least partially dissolved in the perfluorohexane. One preferred agent disclosed comprises a mixture of trifluoromethane dissolved in perfluorohexane. The agents disclosed have zero ozone depletion potential and low toxicity.

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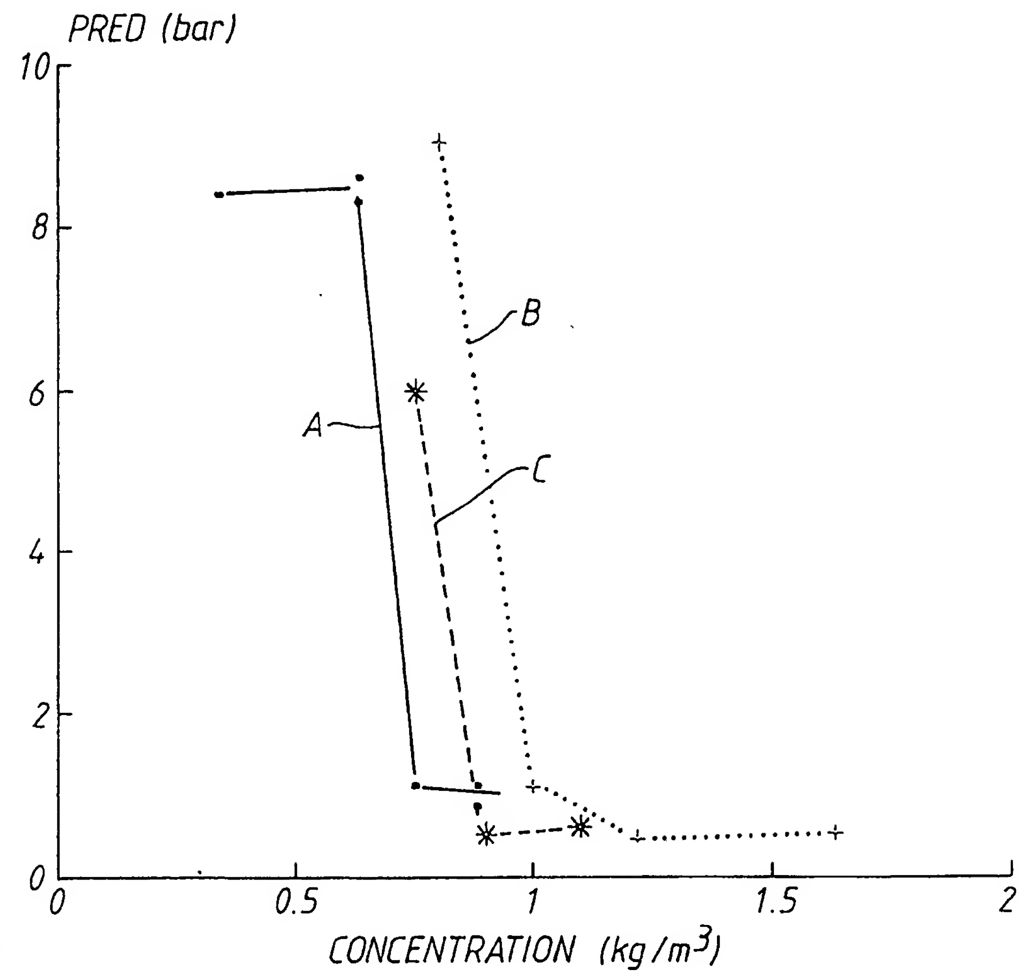
At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.


PRED (bar)
10
8
6
4
2
0
0
0.5
1
1.5
2
CONCENTRATION (kg/m3)
A
B
C

2265309

FIRE EXTINGUISHING AND EXPLOSION SUPPRESSION AGENTS

The invention relates to fire extinguishing and explosion suppression agents. In the following specification and claims, the term "fire suppression" will be used to cover both fire extinguishing and explosion suppression.

According to the invention, there is provided a fire suppression agent, comprising a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above 0C in combination with discharge means for discharging it in atomised form into an area to be protected.

According to the invention, there is further provided a method of suppressing a fire, comprising the step of discharging into the fire, in atomised form, a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above 0C.

According to the invention, there is still further provided a fire suppression agent comprising a mixture of a liquid component and a gaseous component, the liquid component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point above 0C, and the gaseous component comprising one or more non-flammable partially or fully fluorinated hydrocarbons

having a boiling point below OC.

Fire suppression agents embodying the invention will now be described, by way of example only, with reference to certain Examples and to the accompanying drawing which is a Figure showing graphical test results.

Fire suppression agents need to satisfy a number of different requirements. In the first place, of course, they must have efficient fire extinguishing and explosion suppressing capabilities. Secondly, however, they should be environmentally friendly; known extinguishing and suppression agents based on bromofluorocarbons or bromochlorofluorocarbons (Halons) are environmentally damaging and, under the Montreal Protocol on ozone-depleting chemicals and its subsequent amendments, their production has to be phased out by 2000, or earlier in some countries. There is therefore a great need for effective and environmentally acceptable extinguishing and suppression agents. Thirdly, in many cases fire suppression agents have to be used in areas where people are present, such as, for example, in industrial areas or in transport. It is therefore important that the agents to be used should be as harmless as possible to humans.

One Example (Example 1) of a fire suppression agent

comprises perfluorohexane, C_6F_{14}, used in atomised form. The boiling point of perfluorohexane is +58C. It is known for use as a fire suppression agent in the form of a streamed liquid. However, standard laboratory tests of its fire suppression capability when used in this way, against a two-dimensional or surface-type fire, have shown that, in order to produce the same fire suppression capability as a given quantity of Halon 1301, nearly three times as much perfluorohexane is required (when measured in mass or volume terms). Unexpectedly, however, it has been found that, when applied in atomised form, perfluorohexane is particularly effective against three dimensional fires - explosions and rapidly developing fires. When used in this way and in these circumstances, it has been found that a given mass or volume of perfluorohexane can achieve substantially the same suppression capability as substantially the same quantity of Halon 1301.

Preferably, the droplets of perfluorohexane in the atomised discharge have a distribution lying in the region 20 - 200 micrometres. Droplets with this size distribution are large enough to have sufficient momentum to reach the seat of the fire or the developing fire ball in as short a time as possible (typically a few tens of milliseconds). However, they are still small enough to

evaporate in the flame so as to absorb its heat. Atomisation is achieved by forcing the perfluorohexane through a suitably selected nozzle by means of a propellant gas. A suitable propellant gas is nitrogen. Nitrogen is very soluble in perfluorohexane. This solubility aids the atomisation process because, upon discharge of the perfluorohexane under pressure of the gas, the pressure release causes the dissolved nitrogen to come out of solution and this enhances the atomisation process.

Perfluorohexane does not contain chlorine or bromine and does not destroy stratospheric ozone. It has an ozone depletion potential (ODP) of zero. Tests on perfluorocarbons similar to perfluorohexane have shown that they have essentially very low toxicity. Perfluorohexane, when used in the atomised form described above, is thus particularly suitable as a suppression agent for use in crew bay compartments of military vehicles, but is not restricted to such appliances. Other applications could include engine compartments of military vehicles, machinery rooms and compartments in ships, off-shore oil and gas platforms, rail vehicles, civil and military aircraft, aircraft shelters and hangars and the like.

Although in this Example reference has been made to

perfluorohexane, the substance used may be a mixture not only of isomeric perfluorohexanes but also of other perfluorocarbons.

Thus, more generally, perfluorohexane and other perfluorocarbons (i.e. fully fluorinated hydrocarbons) or partially fluorinated hydrocarbons (i.e. high boiling point hydrofluorocarbons) or mixtures and isomers of them, having boiling points above 0 C, and preferably in the range +20 to +150 C, could be used in the manner explained above in Example 1. Suitable perfluorocarbons and hydrofluorocarbons are:-

TABLE 1

perfluoropentane	$CF_3(CF_2)_3CF_3$	(+29C)
perfluoroheptane	$CF_3(CF_2)_5CF_3$	(+83C)
perfluoroctane	$CF_3(CF_2)_6CF_3$	(+105C)
perfluorononane	$CF_3(CF_2)_7CF_3$	(+125C)
1H-tridecafluoro-n-hexane	$CF_3(CF_2)_4CHF_2$	(+72)
1-trifluoromethyl-2H-decafluoro-n-heptane	CF3CH(CF3)CF2CF2CF3	(+55)
1H-pentadecafluoro-n-heptane	$CF_3(CF_2)_5CHF_2$	(+94)
1H-heptadecafluoro-n-octane	$CF_3(CF_2)_6CHF_2$	(+118)
4H,5H-hexadecafluoro-n-octane	$CF_3(CF_2)_2(CHF)_2(CF_2)_2CF_3$	(+112)

The figures in brackets represent the respective boiling points. These substances also have zero ODP and are believed to have low toxicity when used in the applications referred to.

Instead of nitrogen as the pressurising gas, another inert gas could be used, such as argon, helium or carbon dioxide.

A second Example (Example 2) of a suppression agent embodying the invention comprises a mixture of a high boiling point perfluorocarbon, such as perfluorohexane, with a low boiling point fluorinated hydrofluorocarbon. A suitable hydrofluorocarbon is trifluoromethane (CHF_3). Trifluoromethane has a boiling point of -82C and, as a gas, is very soluble in perfluorohexane. It is found that such a mixture has very effective suppression capabilities. A mixture containing perfluorohexane and trifluoromethane in a mole ratio of 2:1 (i.e. about 9% by weight of trifluoromethane) has been found to have a suppression capability of the same order as Halon 1301. However, it is not believed that the dissolved gaseous trifluoromethane acts in the same way as the pressurising gas (e.g. nitrogen) referred to above (for atomising the perfluorohexane). It is believed that the trifluoromethane primarily acts, upon discharge of the mixture, by the resultant evaporation effect which causes

the perfluorohexane to be rapidly and significantly cooled, and it is this cooling effect which primarily provides the beneficial suppression ability.

In the mixture described, the perfluorohexane could be replaced by (or mixed with) one or more other partially or fully fluorinated hydrocarbons with boiling points above 0 C and preferably in the range +20C to +150C, such as those listed in Table 1 above. Furthermore, the trifluoromethane could be replaced by (or mixed with) one or more other hydrofluorocarbons and/or with one or more perfluorocarbons having a boiling point below 0 C. Examples of such other hydrofluorocarbons and perfluorocarbons are:-

TABLE 2

difluoromethane	CH_2F_2	(-52C)
pentafluoroethane	CF_3CHF_2	(-49C)
perfluoroethane	CF_3CF_3	(-78C)
perfluoropropane	$CF_3CF_2CF_3$	(-37C)
perfluorobutane	$CF_3CF_2CF_2CF_3$	(-2C)
perfluorocyclobutane	cyclo-C_4F_8	(-6C)
1,1,1,2-tetrafluoroethane	CF_3CH_2F	(-27C)
1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3	(-17C)

Again, the temperature figures in brackets indicate the respective boiling points of the substances.

Like the perfluorocarbons, these hydrofluorocarbons have zero ODP and are believed to be relatively non-toxic when used in the applications referred to.

The Figure shows the results of performance tests carried out for comparing the explosion suppression capabilities of suppression agents according to Examples 1 and 2 with each other and with Halon 1301.

The tests were carried out using a test vessel of $6.2m^3$ in volume. A predetermined quantity, about 1 litre, of diesel fuel, prewarmed to 90C, is sprayed into the vessel and ignited. The incipient explosion is detected by the rise in pressure (although this can be done optically by means of optical flame detectors known to those skilled in the art). When the pressure from the steadily growing explosion fireball exceeds 0.025 bar, the contacts of a pressure switch are closed automatically, triggering discharge of the suppressant from one or more rapid-action suppressors into the test vessel. A measure of the suppressant action is given by the maximum pressure (Pred) attained in the vessel. The lower this parameter, the better is the suppression. The horizontal axis plots the

concentration of the injected suppression agent (in kilograms of agent per cubic metre of the test vessel). In all of these tests, the fluorinated hydrocarbons contained within the suppressors were pressurised to 52 bar with nitrogen gas.

Pred figures of less than 1 bar are considered to represent satisfactory suppression; figures over 1 bar are considered to represent failed suppression.

Curve A shows the results obtained using Halon 1301, while curve B relates to atomised perfluorohexane (Example 1) and curve C relates to the mixture of perfluorohexane and trifluoromethane (Example 2) in a 2:1 mole ratio (i.e. about 9% by weight of trifluoromethane). The Figure shows that the agents of Examples 1 and 2 give very effective suppression when used in concentrations only slightly greater than Halon 1301.

Similar results are obtained using other mixtures of perfluorohexane and trifluoromethane, for example 1:1 or 1:2 mole ratios.

CLAIMS

1. A fire suppression agent, comprising a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above OC in combination with discharge means for discharging it in atomised form into an area to be protected.

2. An agent according to claim 1, in which the discharge means comprises a pressurising gas.

3. A method of suppressing a fire, comprising the step of discharging into the fire, in atomised form, a non-flammable partially or fully fluorinated hydrocarbon having a boiling point above OC.

4. A method according to claim 3, including the step of atomising the non-flammable partially or fully fluorinated hydrocarbon by means of a pressurising gas.

5. An agent or method according to claim 2 or 4, in which the pressurising gas at least partially dissolved in the non-flammable partially or fully fluorinated hydrocarbon.

6. An agent or method according to any one of claims 2,4 and 5, in which the pressurising gas is nitrogen.

7. An agent or method according to any one of claims 2,4 and 5, in which the pressurising gas is selected from the group comprising nitrogen, argon, helium, and carbon dioxide.

8. An agent or method according to any preceding claim, in which the atomised discharge has a droplet size distribution in the range 20-200 micrometres.

9. An agent or method according to any preceding claim, in which the non-flammable partially or fully fluorinated hydrocarbon comprises perfluorohexane.

10. An agent or method according to any one of claims 1 to 8, in which the non-flammable partially or fully fluorinated hydrocarbon comprises one or more of the following: perfluoropentane, perfluorohexane; perfluoroheptane; perfluoroctane; and perfluorononane.

11. A fire suppression agent comprising a mixture of a liquid component and a gaseous component, the liquid component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point above OC, and the gaseous component comprising one or more non-flammable partially or fully fluorinated hydrocarbons having a boiling point below OC.

12. An agent according to claim 11, in which the liquid component comprises perfluorohexane and the gaseous component comprises trifluoromethane.

13. An agent according to claim 12, in which the mole ratio of the perfluorohexane and the trifluoromethane in the mixture is approximately 2:1.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number

9206204.1

Relevant Technical fields

(i) UK Cl (Edition K) A5A (A1, A2, A6, A9)

(ii) Int Cl (Edition 5) A62C, A62D

Databases (see over)

(i) UK Patent Office

(ii)

Search Examiner

DR D ELSY

Date of Search

21 JULY 1992

Documents considered relevant following a search in respect of claims 1-10

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0460990 A1 (ATOCHEM) - see claims and page 2 lines 43-44	1-10
X	WO 92/01491 A1 (GREAT LAKES) - see claims	1-7
X	WO 91/02564 (GREAT LAKES) - see claims and page 7 lines 19-28	1-7

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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